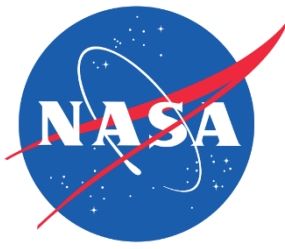


Radiation Effects on Lithium CF_x Batteries for Future Landers



Keith J. Billings, Ratnakumar Bugga, Keith B. Chin, John-Paul Jones,
Simon C. Jones, Charlie Krause, Adam Lawrence, Raymond
Ontiveros, Jasmina Pasalic, Marshall C. Smart, and William C. West,
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Electrochemical Technologies Group

Jet Propulsion Laboratory, California Institute of Technology
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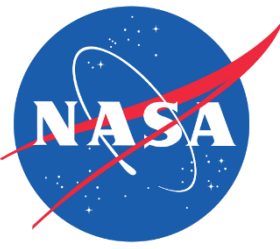
Space Power Workshop

Los Angeles, CA
Thursday, April 23, 2018

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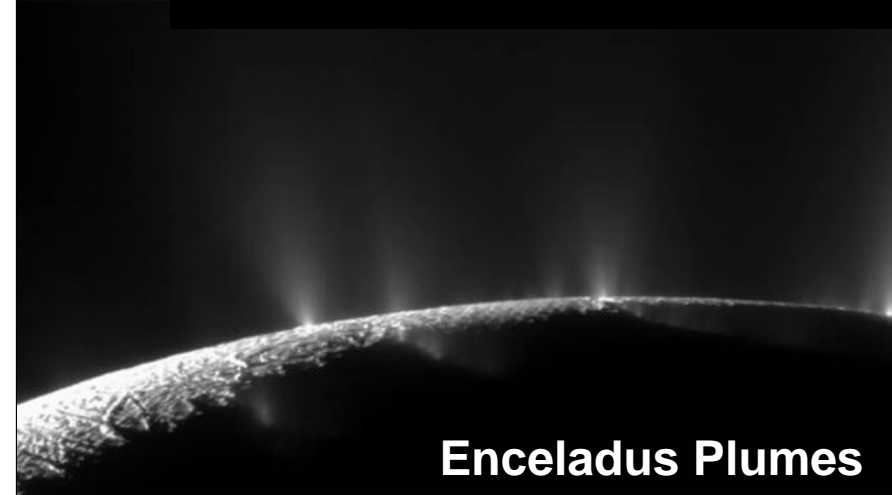
Increasing Interest in a lander for “Ocean Worlds”



A potential Europa Lander could use primary batteries operating for weeks vs. hours



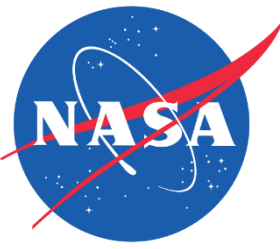
Europa



Enceladus Plumes



Titan Lakes

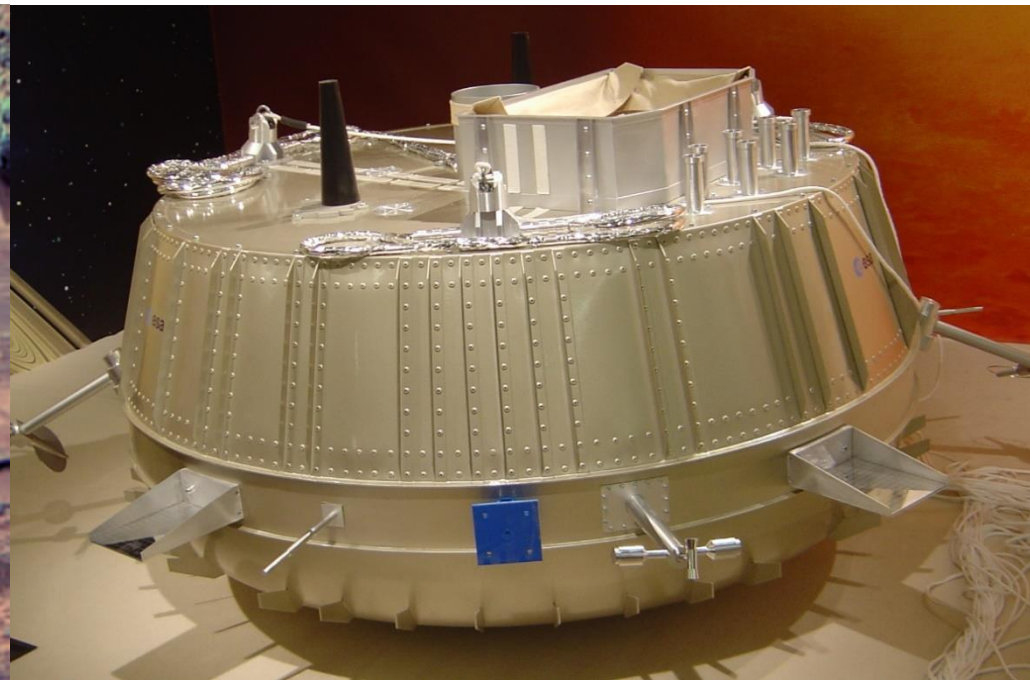
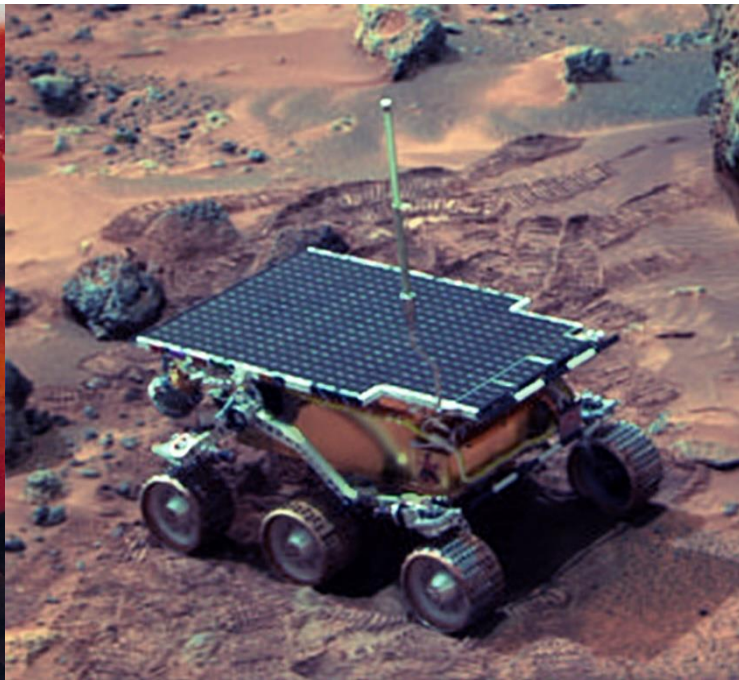
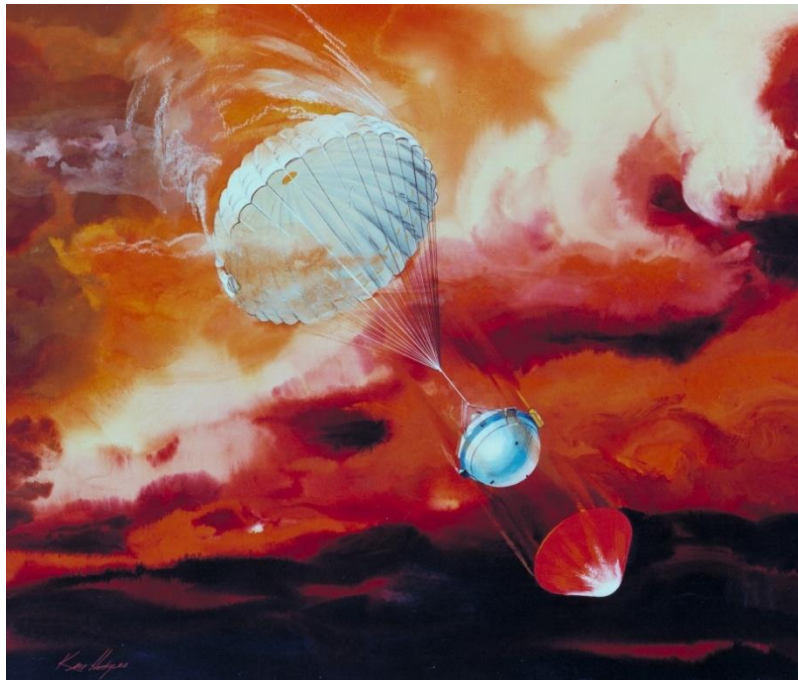


Three Examples of Primary Batteries for Space

Galileo Probe 1989: Li/SO_2
~580 Wh
58 minutes

Sojourner Rover 1996: Li/SOCl_2
432 Wh
56 days (PV + battery)

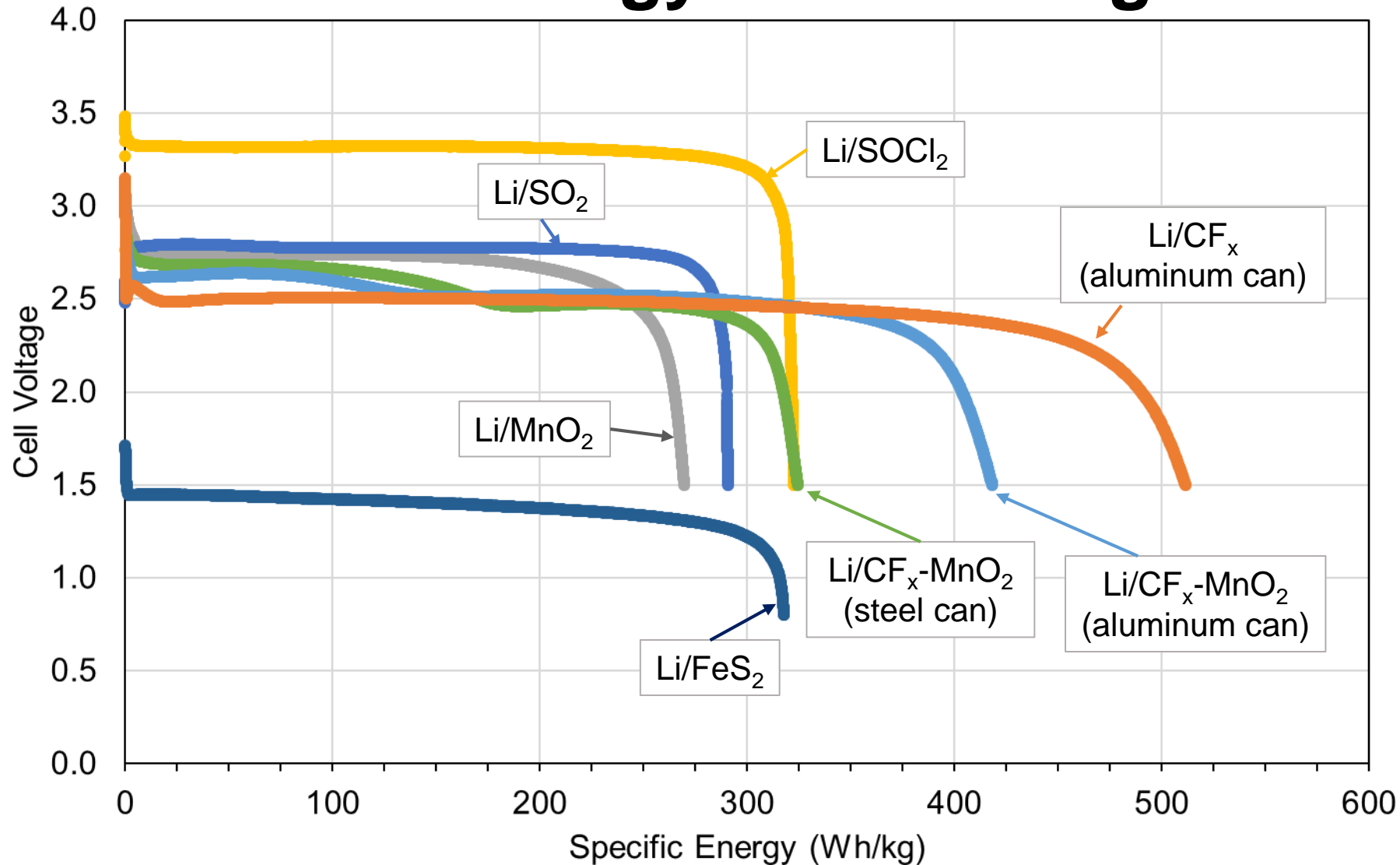
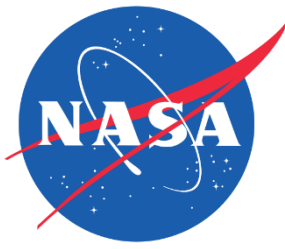
Huygens Probe 2004: Li/SO_2
~2700 Wh
153 minutes



A Europa Lander could require at least 480 hours of operation on battery power alone, therefore, high specific energy is critical to achieving mission objectives

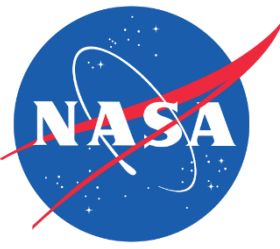
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Li/CF_x cells provide 50% more energy than heritage cells



- Discharged at the same condition
- 0 °C, 250 mA
- Li/FeS₂ discharged at 100 mA due to size (AA instead of D)
- 2 Li/FeS₂ cells could be connected in series to provide comparable voltage

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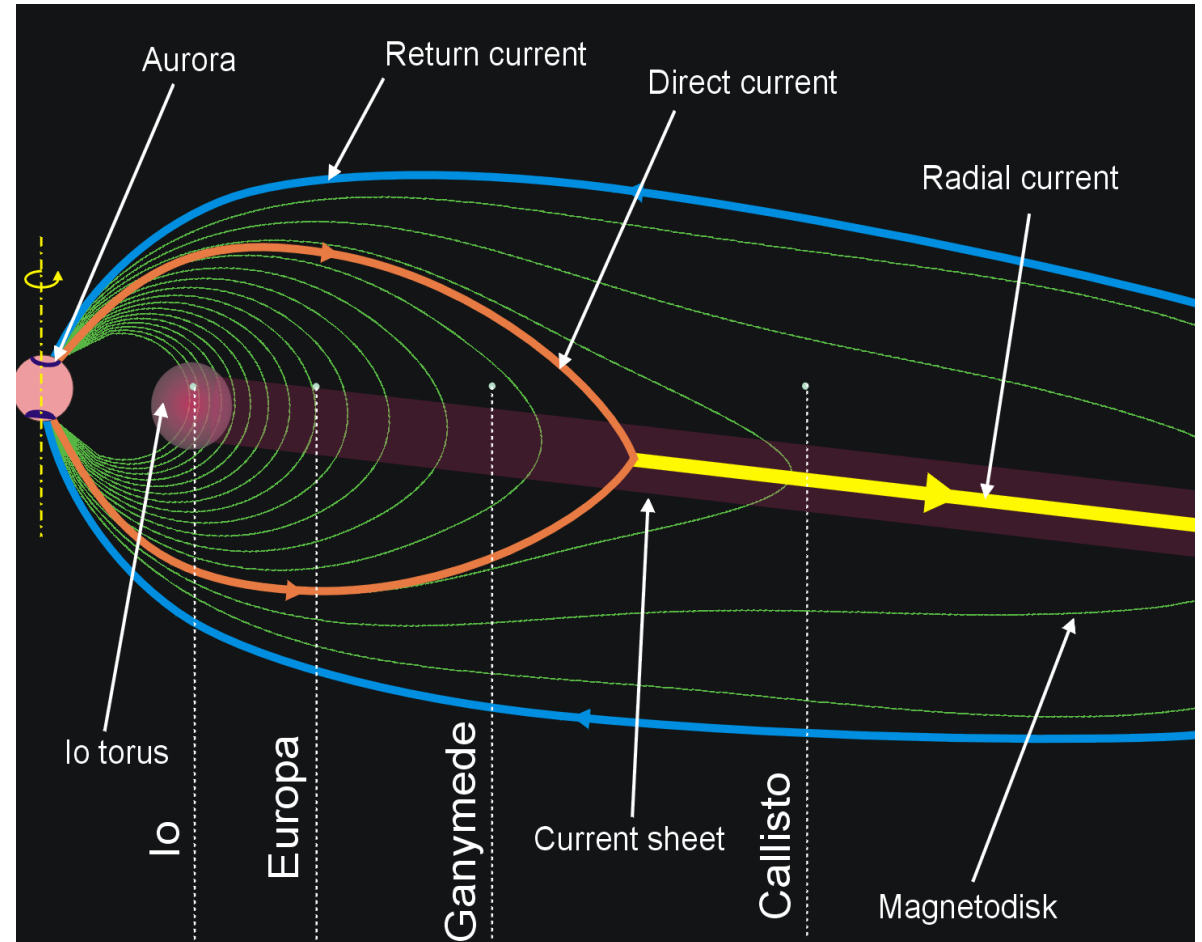


Radiation Testing

- Jupiter generates a high radiation environment
- Europa is directly in the path
- Possible sterilization procedure for planetary protection
- JPL high dose rate ^{60}Co source
 - 1.3 MeV gamma rays
 - ~200 rad/s
 - 1 MRad up to 15 MRad

Test articles:

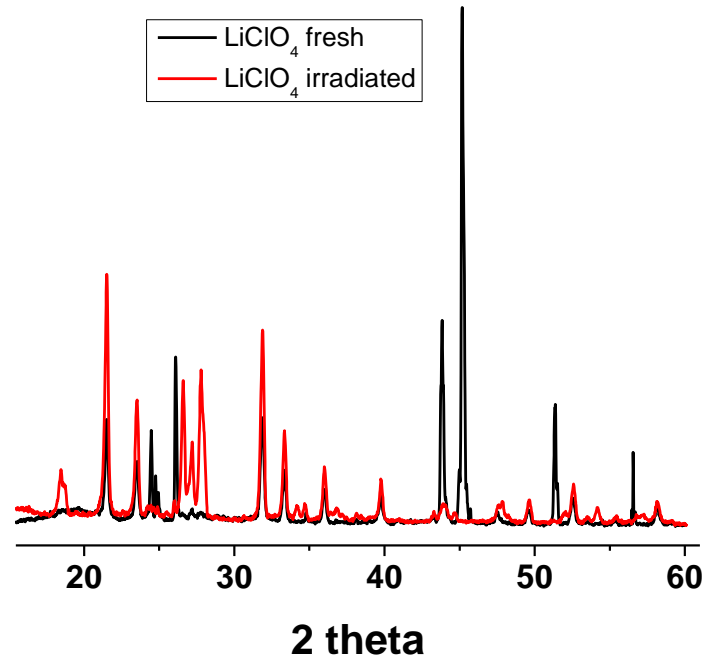
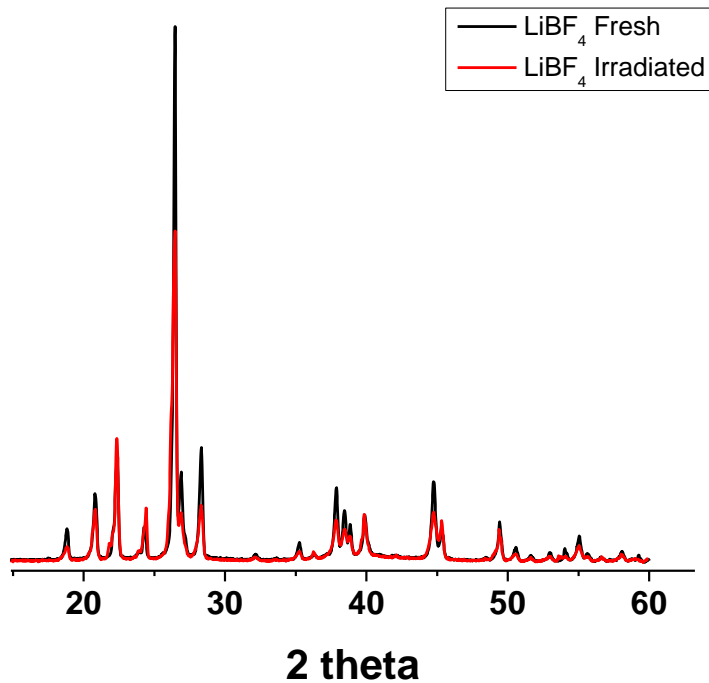
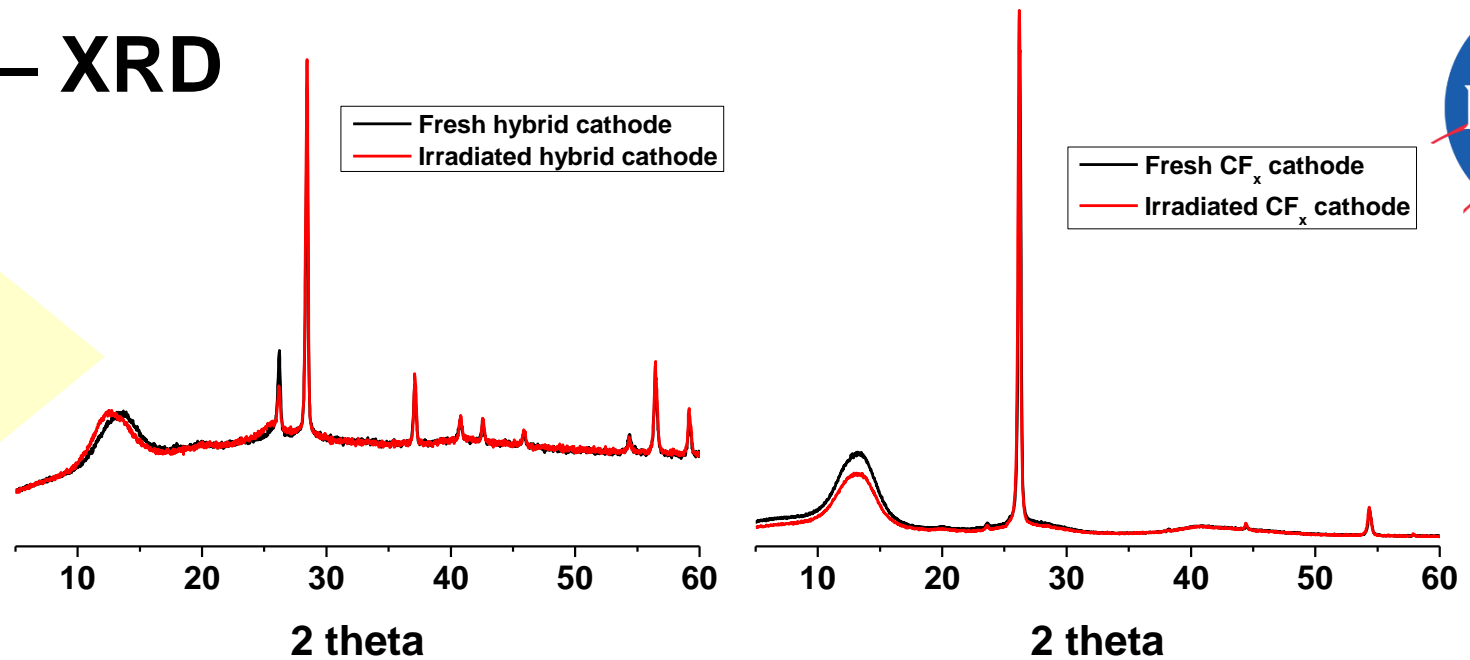
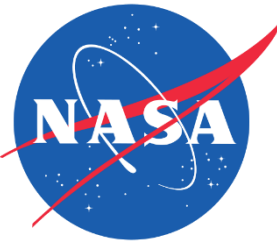
- Rayovac Li/CF_x D-cells
 - LiBF₄ in PC+DME
- Eagle-Picher Li/CF_x-MnO₂ D-cells
 - LiClO₄ in PC+DME+THF
- 3-electrode Li/CF_x cells
- Cell components (cathode materials, salts, electrolytes, separators)



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<https://commons.wikimedia.org/w/index.php?curid=6555923>

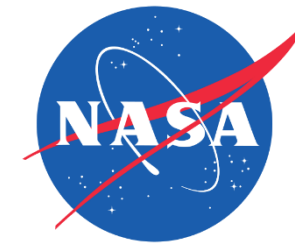
Materials testing – XRD analysis

Pure CF_x and $\text{CF}_x\text{-MnO}_2$ cathodes do not change significantly during exposure to 10 MRad

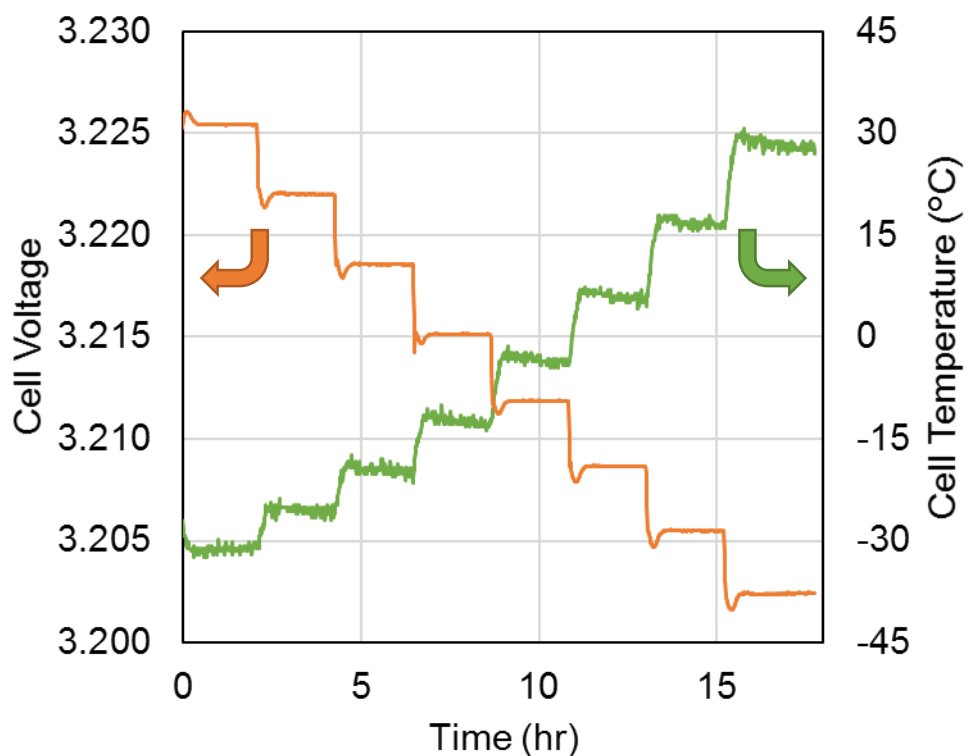


LiClO_4 appears to change due to 10 MRad, while LiBF_4 does not

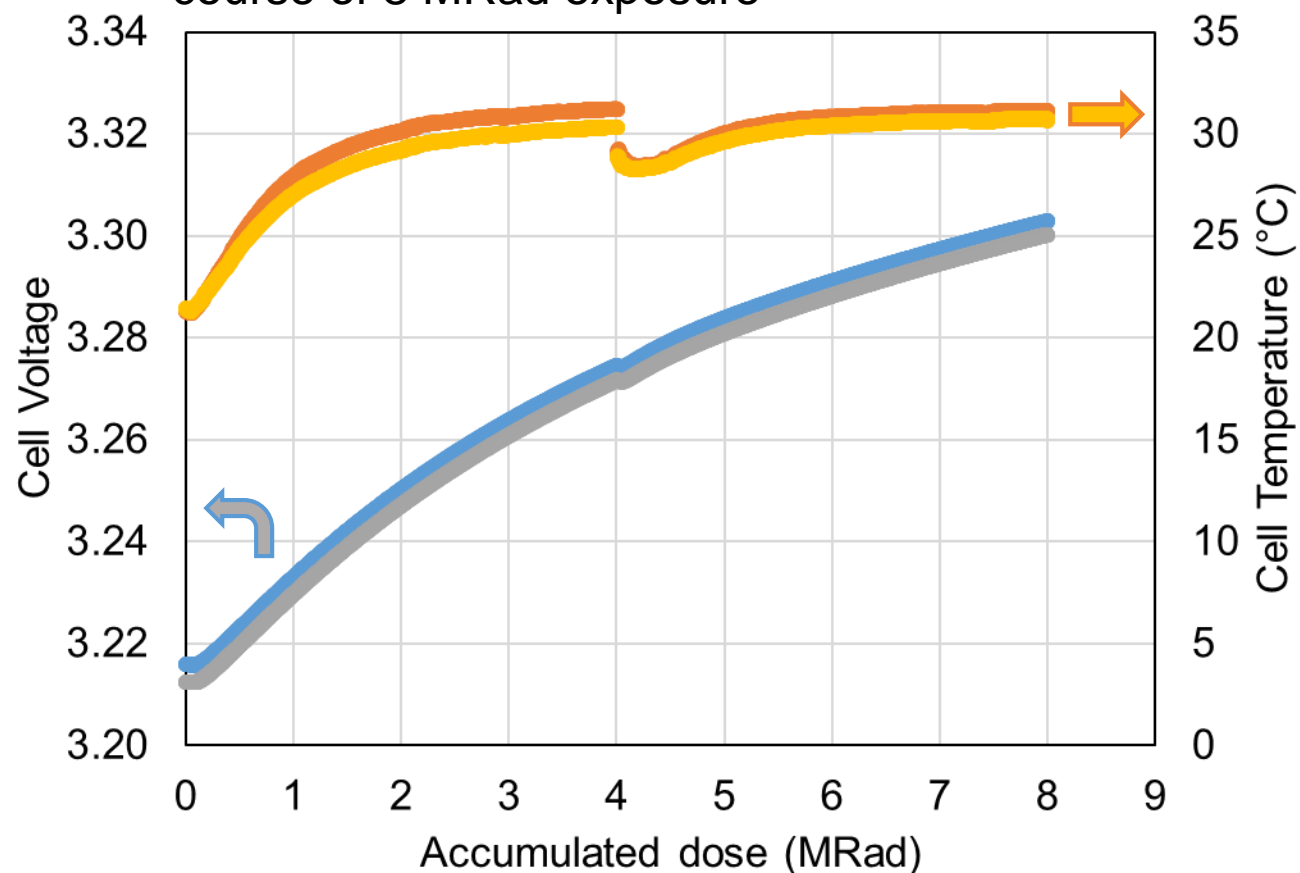
Li/CF_x-MnO₂ cell voltages increase during radiation exposure



Temperature rise does not correlate with voltage increase in the absence of radiation

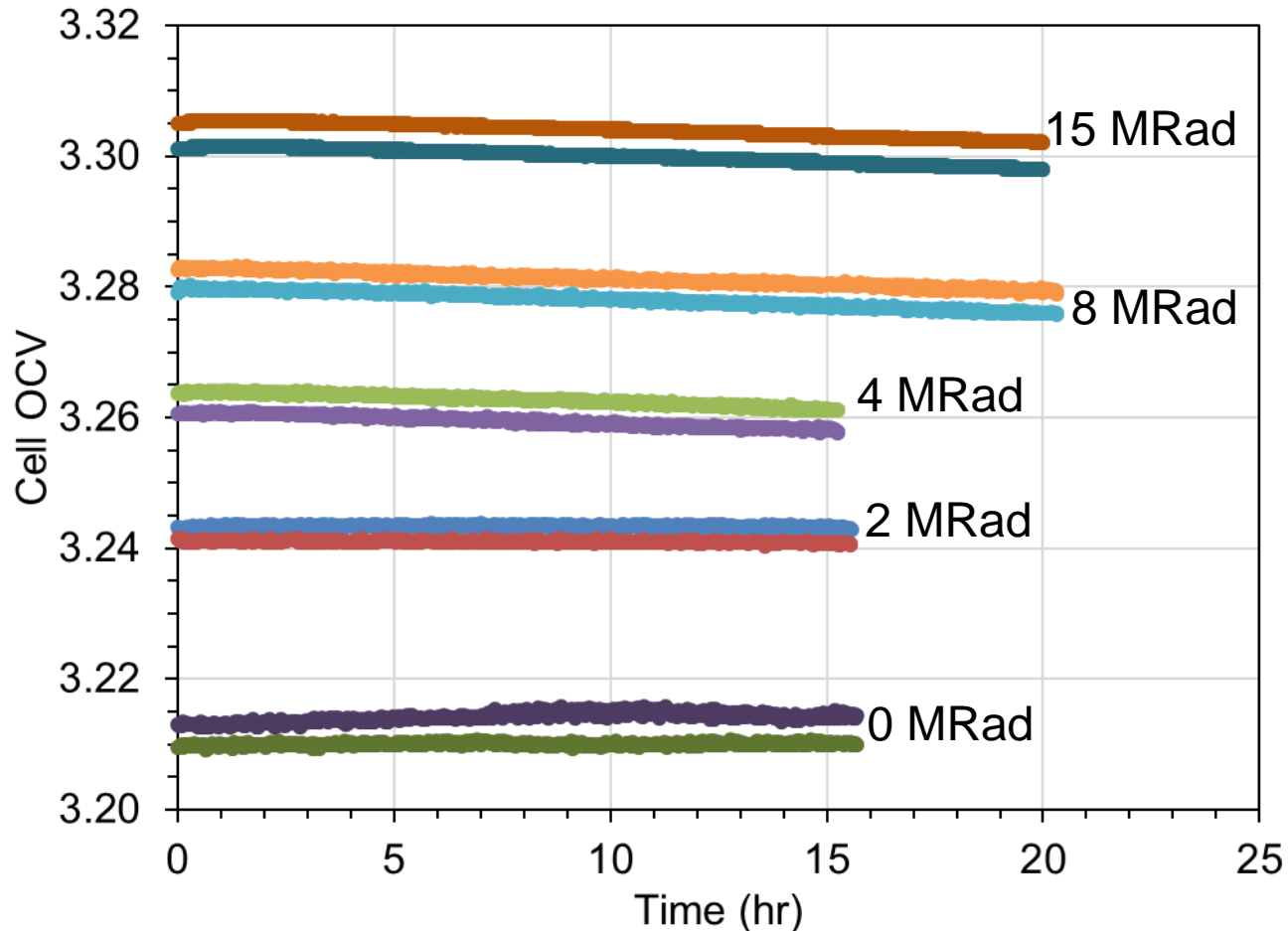
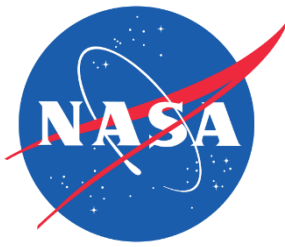


Cells increase by ~100 mV and 9 °C over the course of 8 MRad exposure

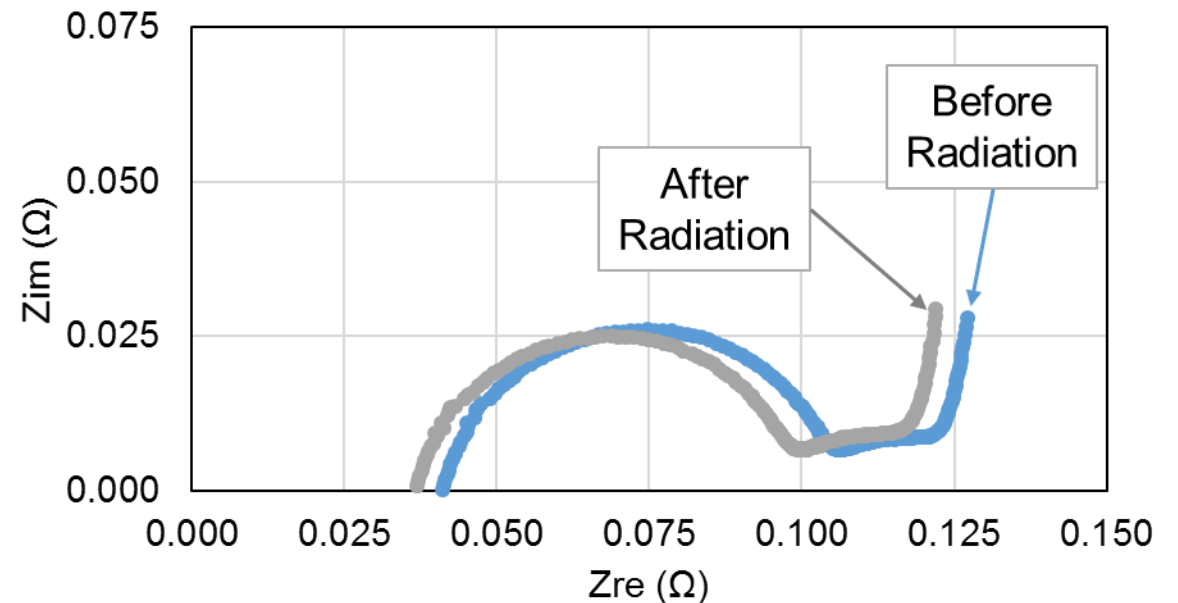


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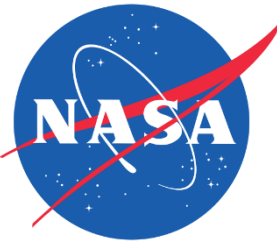
Rest OCV and Impedance Analysis of Li/CF_x-MnO₂ Cells



- OCV monitored for >15 hours
- Linear regression analysis shows a slight voltage drop (**0.18 to 0.2 mV/hr**) for higher dose cells (4, 8, 15 MRad)
- No change in impedance after radiation
 - Spectrum slightly shifted due to connections

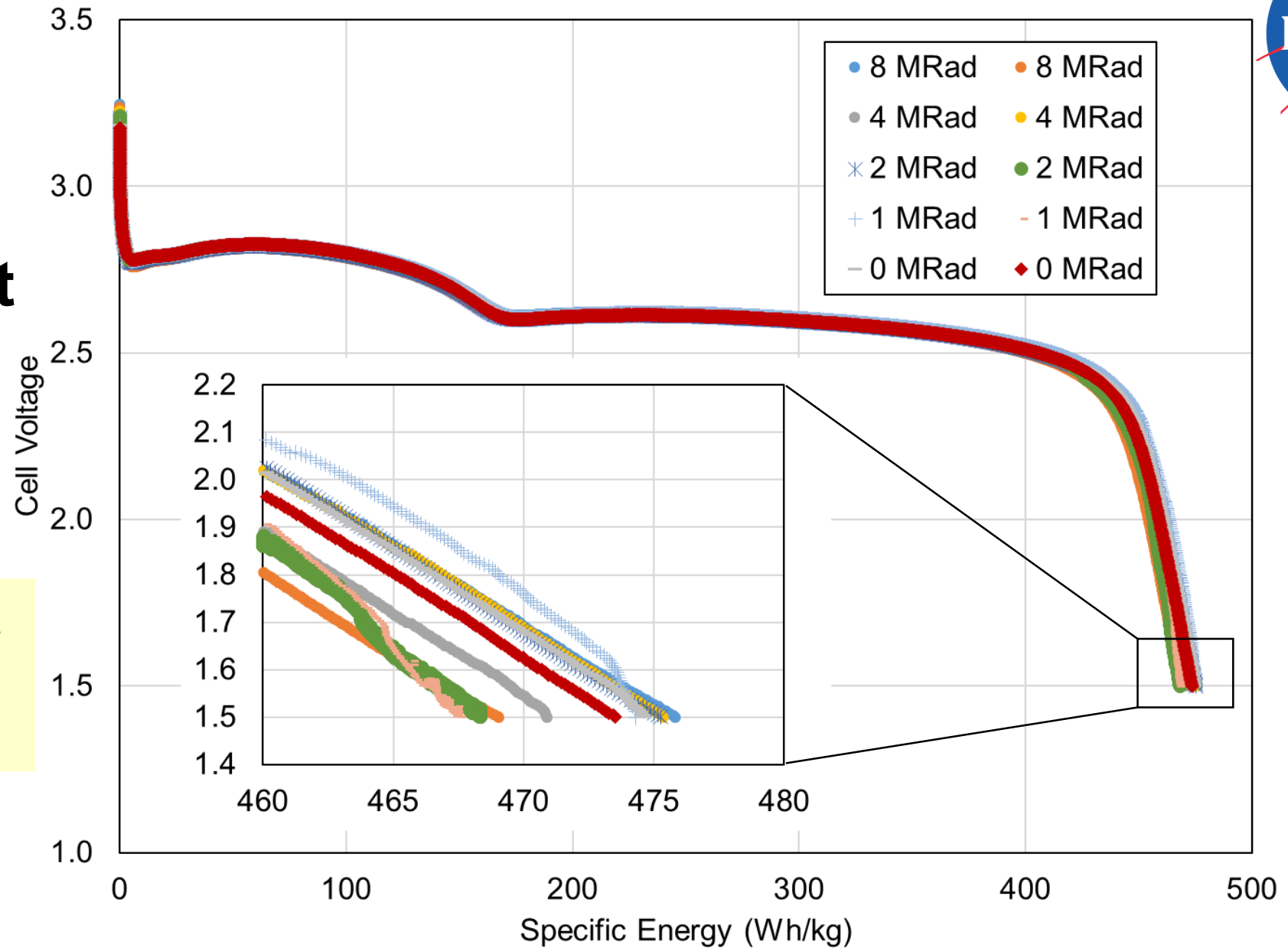


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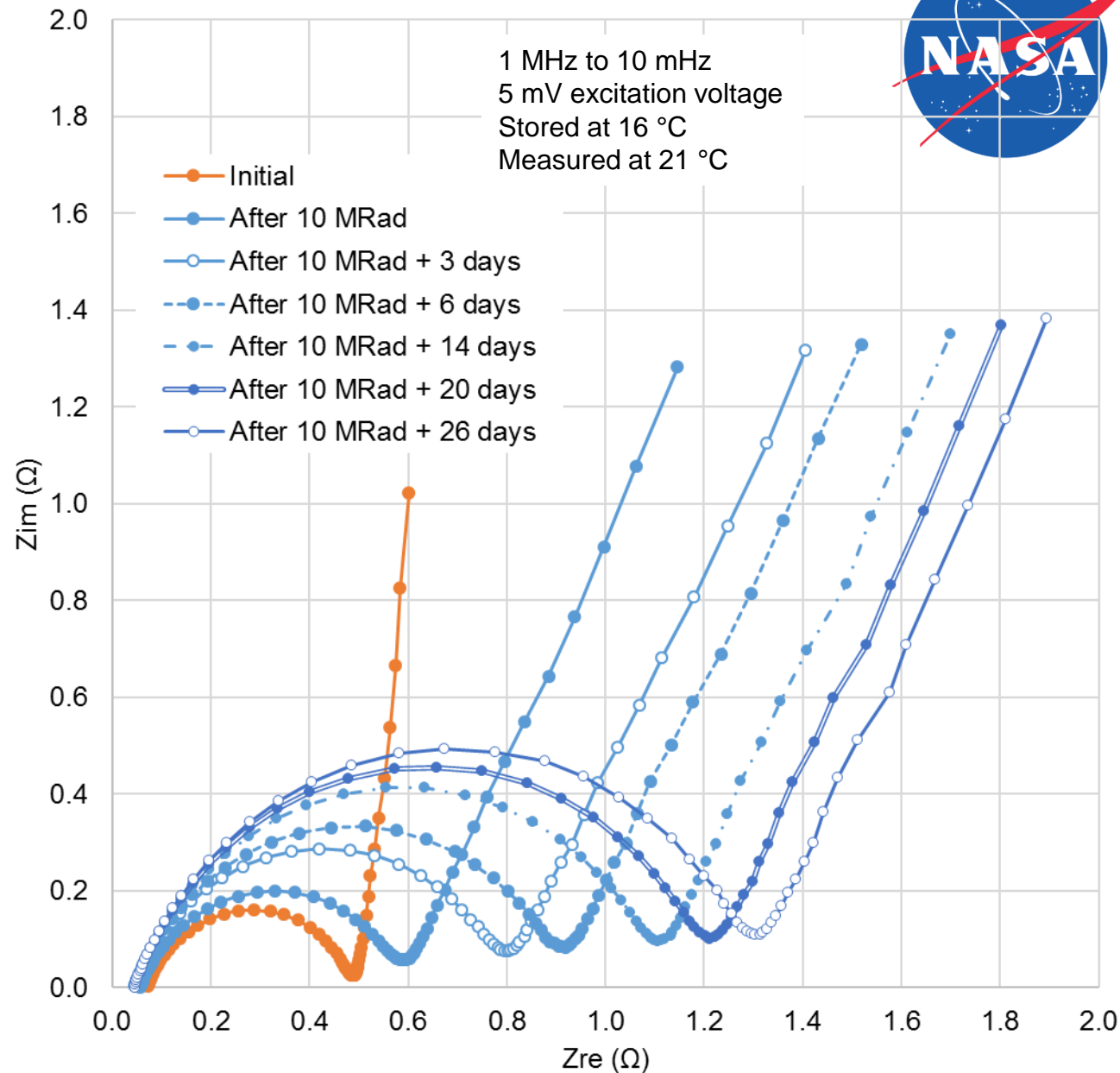
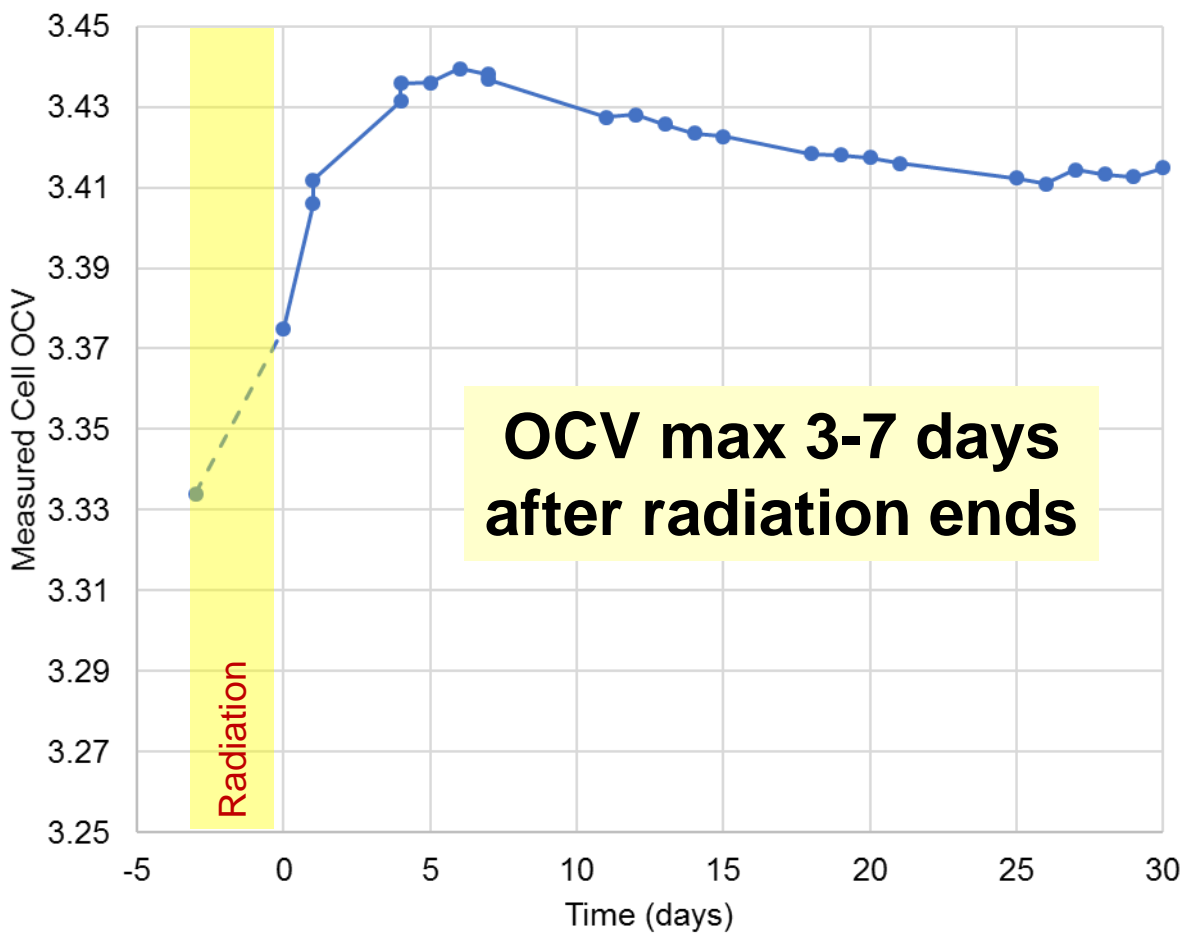
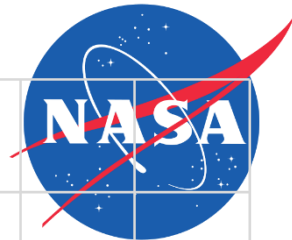


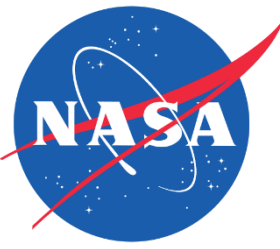
Li/CF_x-MnO₂ Radiation cell discharge performance at 250 mA, 21 °C

Radiation does not
appear to impact
capacity or energy



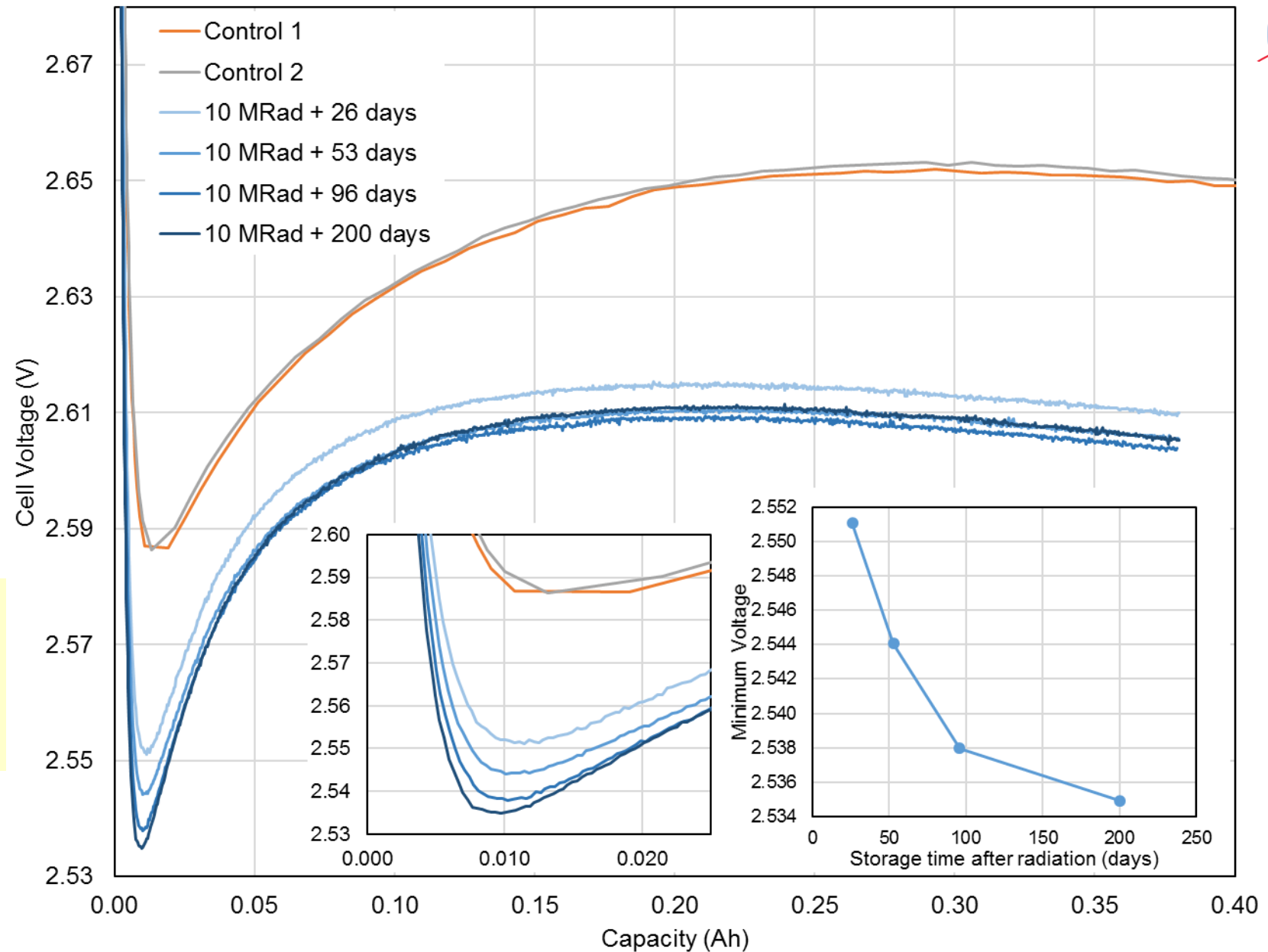
OCV and Impedance change drastically for Li/CF_x D-cell after 10 MRad





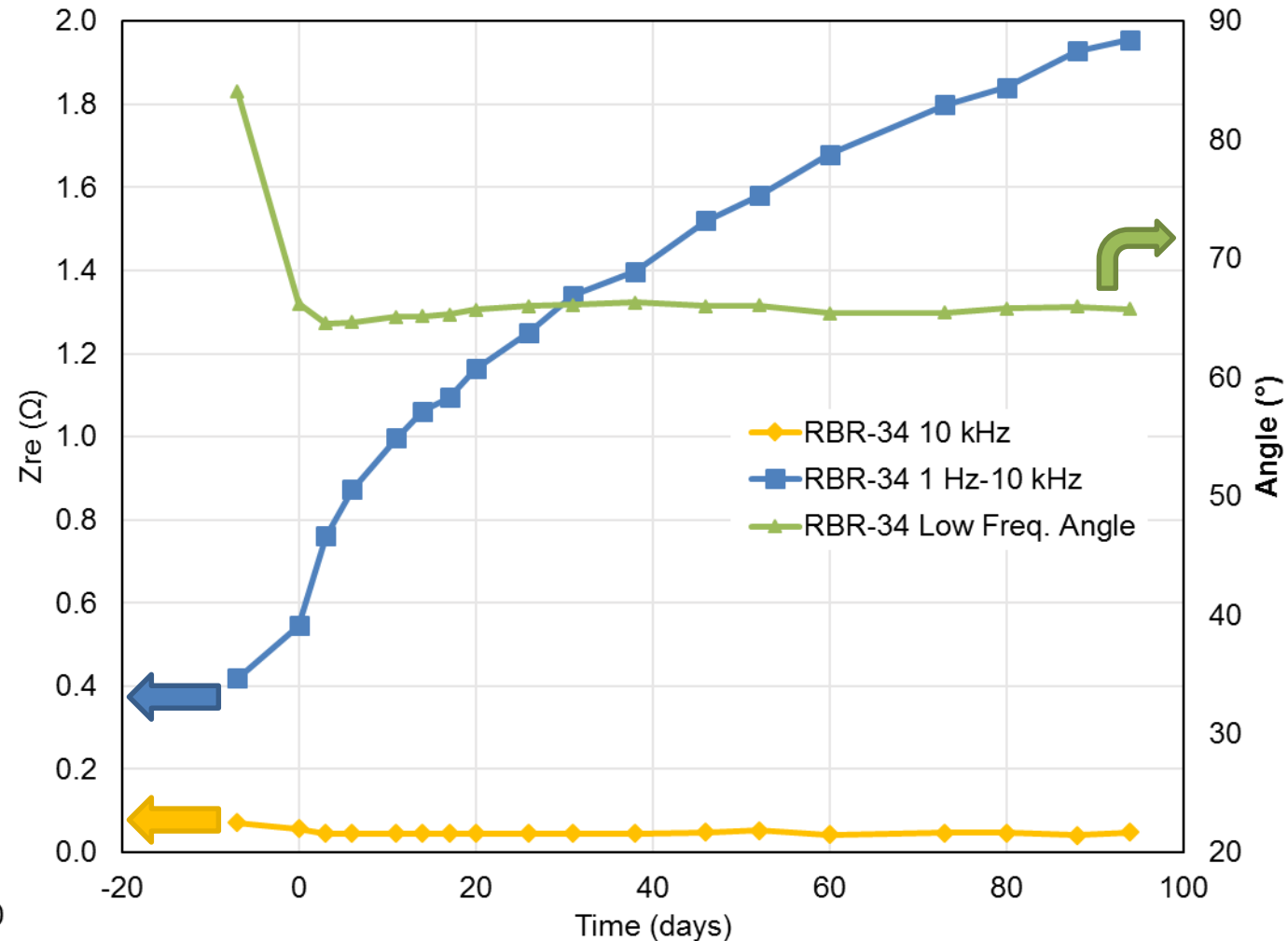
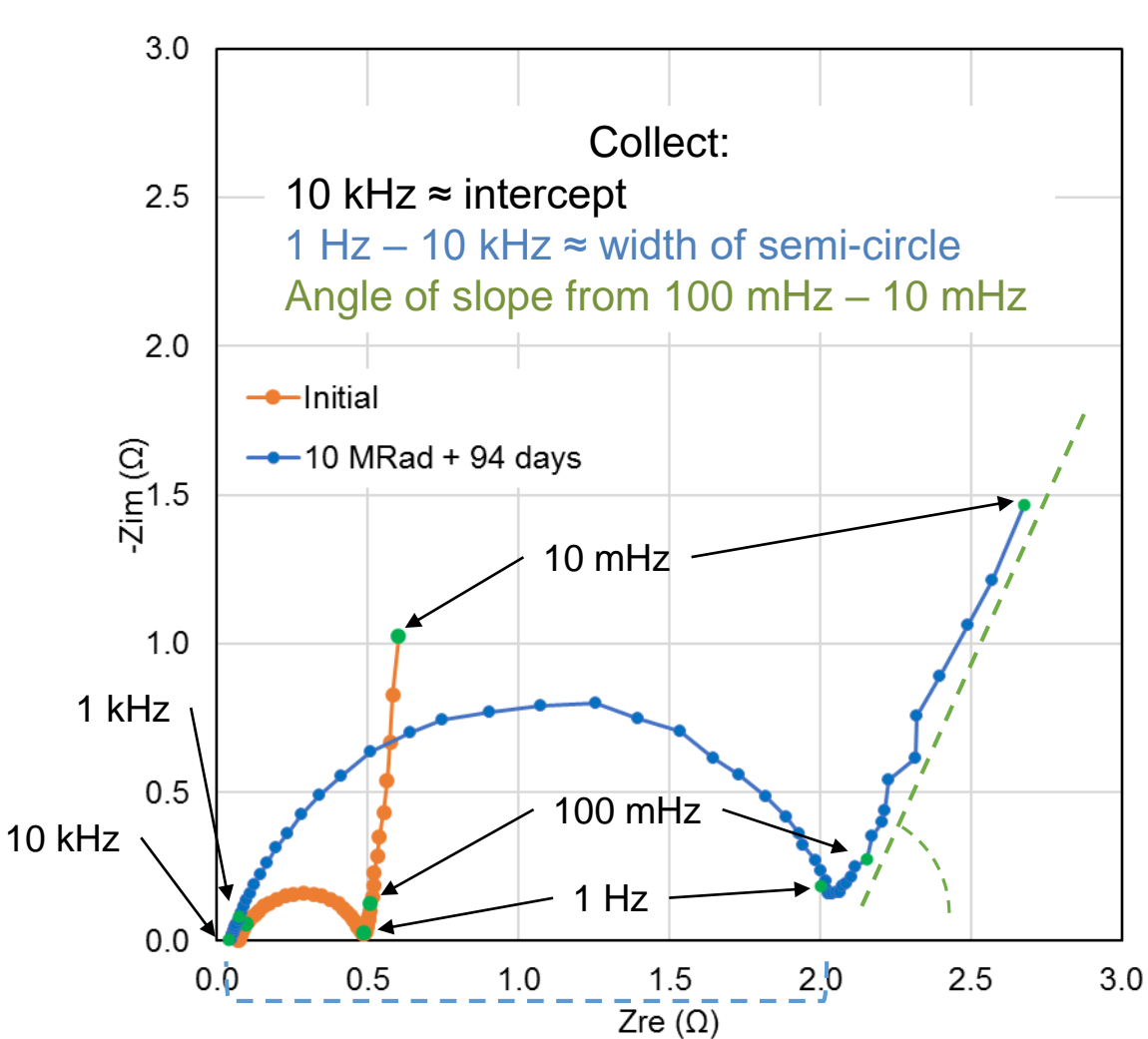
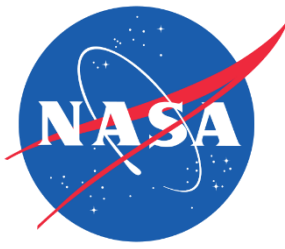
**Discharge 2%
of capacity at
250 mA, 21 °C
to remove any
film grown
during
radiation**

**Initial voltage drop
affected by time
after radiation**



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Quantifying EIS changes over time for Li/CF_x cells

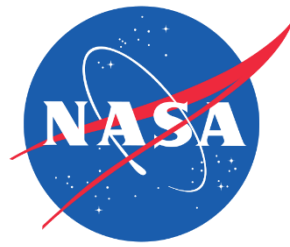


1 MHz to 10 mHz
5 mV excitation voltage

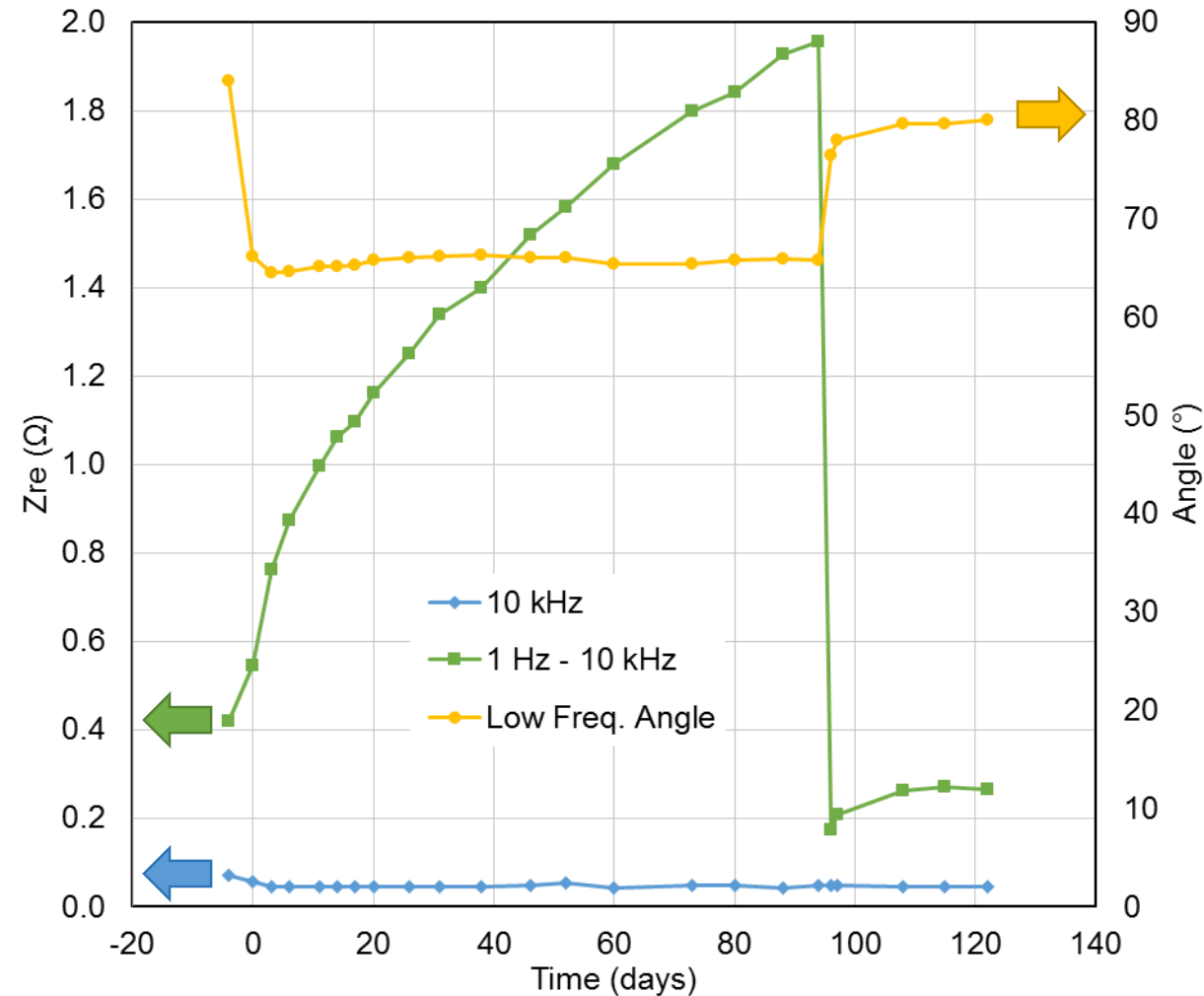
Stored at 16 °C
Measured at 21 °C

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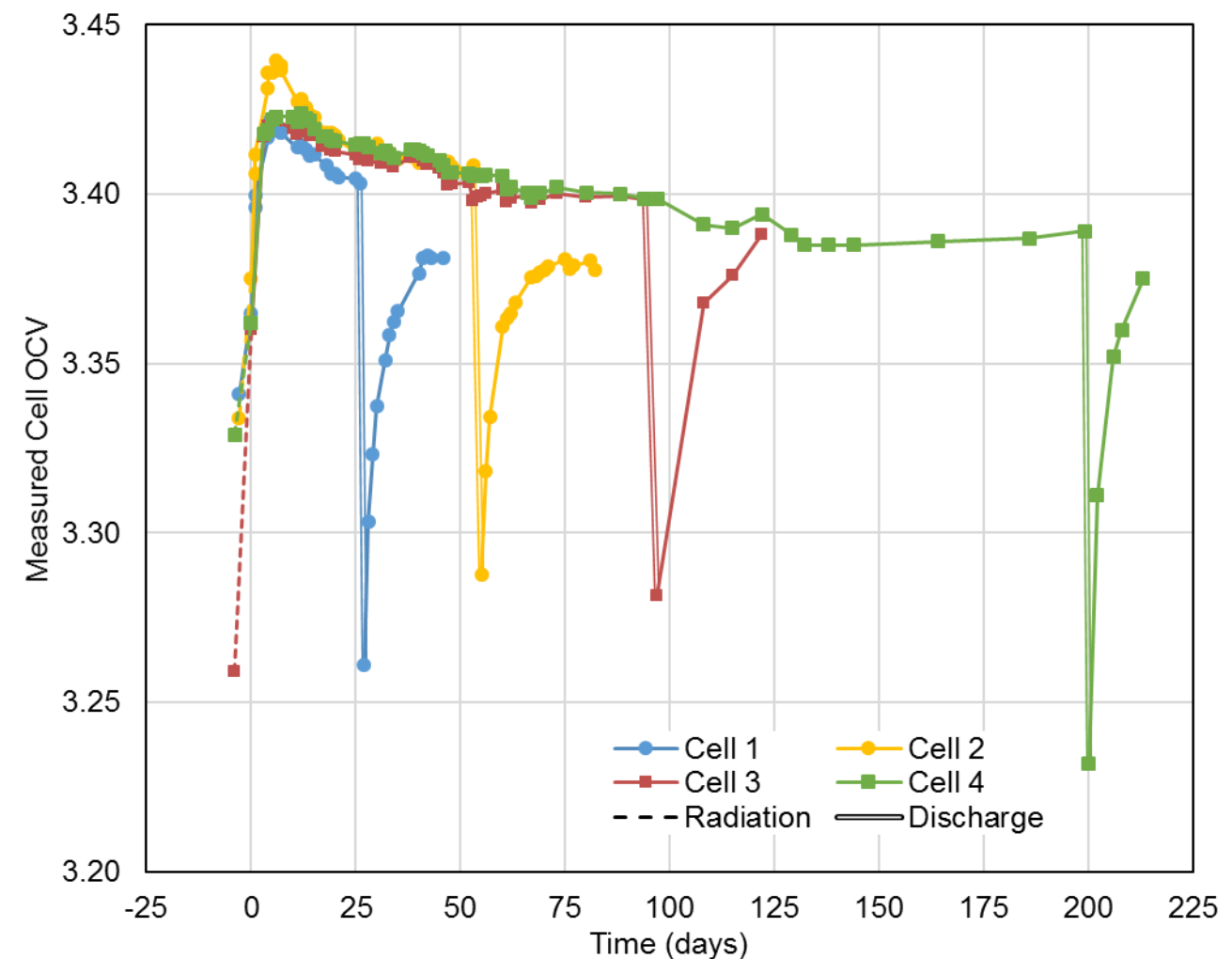
2% discharge effects on EIS and OCV



Semi-circle width decreases
Low freq. angle becomes steeper



OCV remains elevated
after discharge



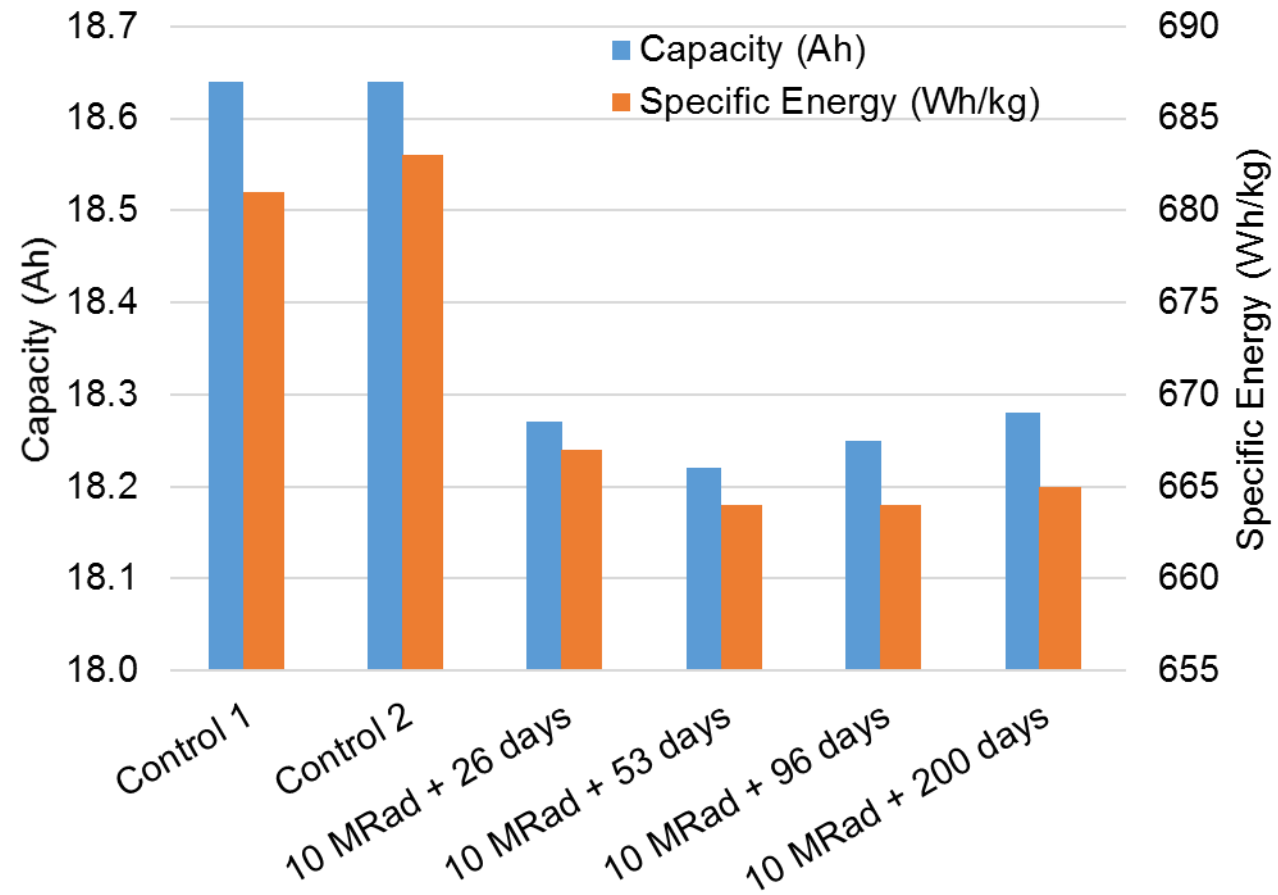
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Total capacity and specific energy for Li/CF_x

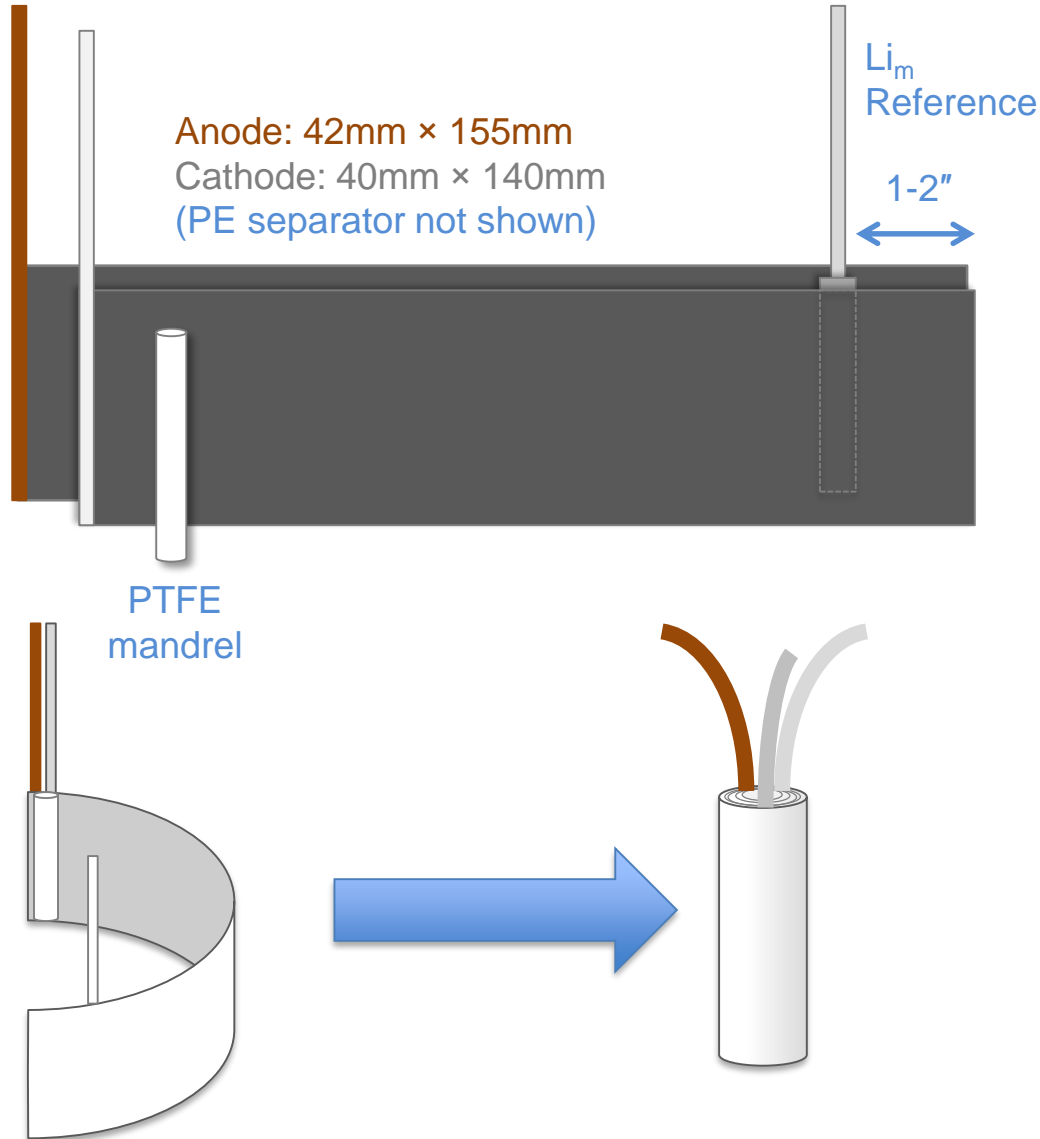
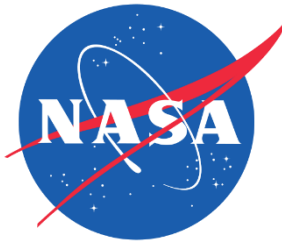
D-cells drops by ~2% after radiation



	Capacity (Ah)	Specific Energy (Wh/kg)
Non-irradiated average:	18.64	682
10 MRad average:	18.28	667
Drop:	1.94%	2.23%



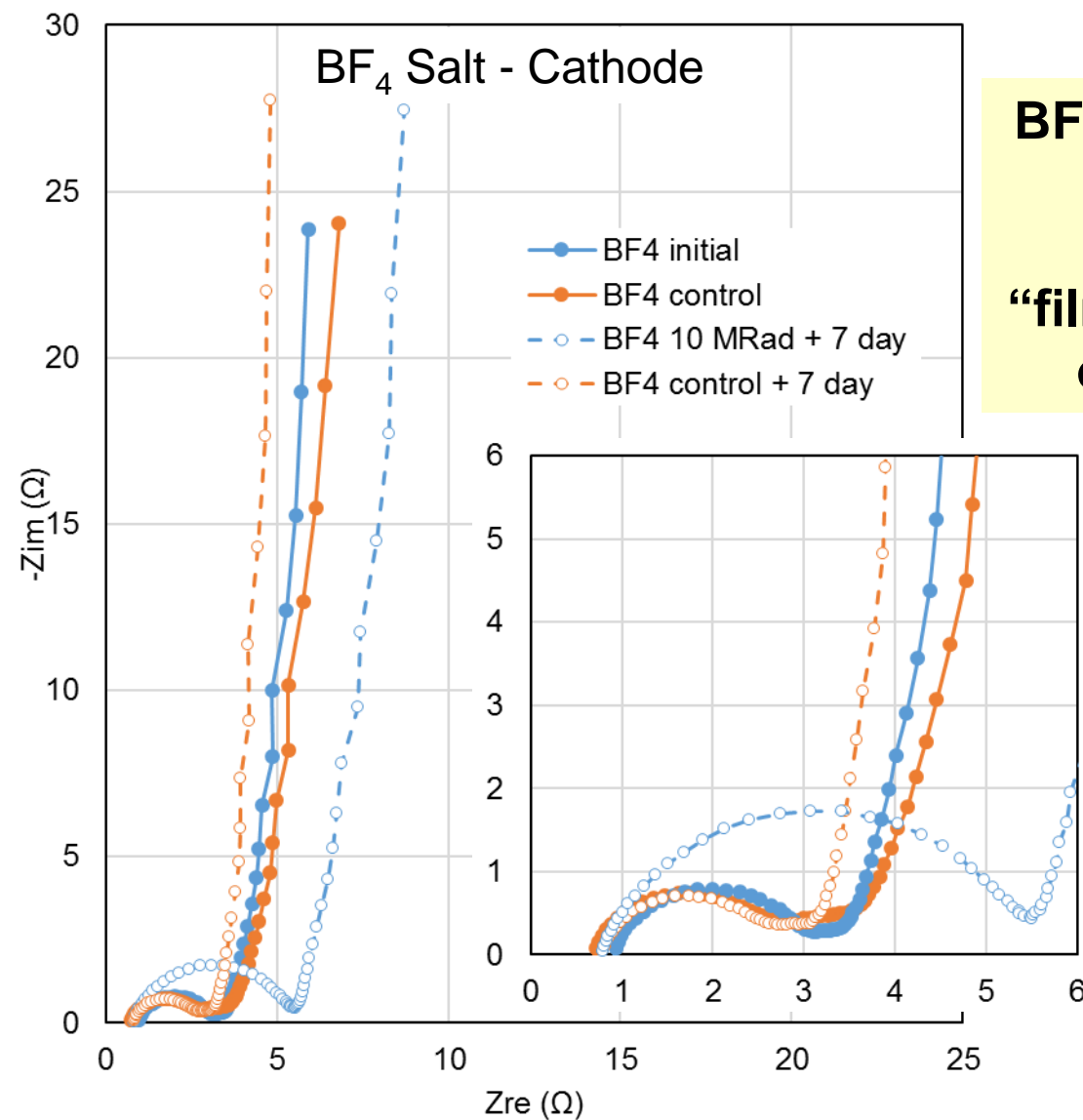
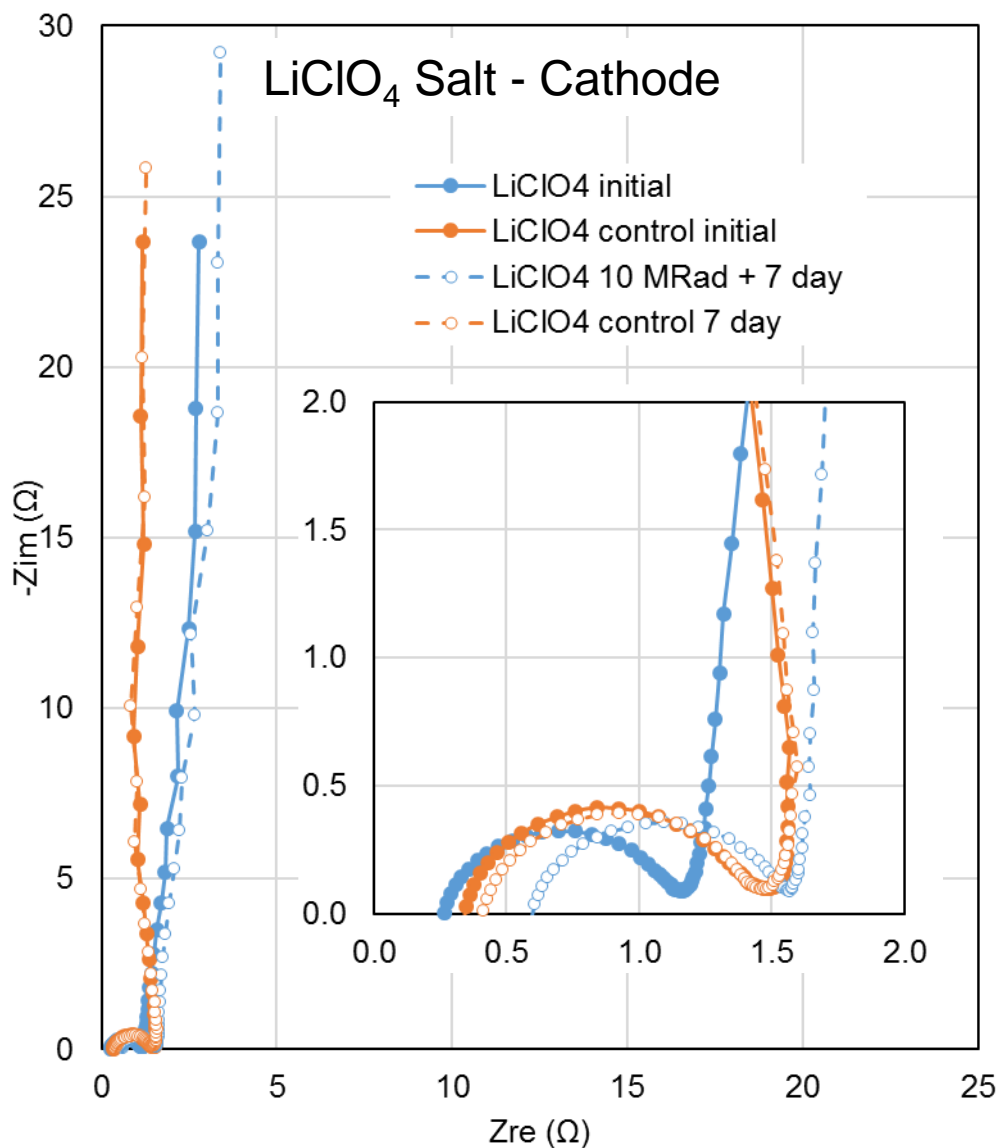
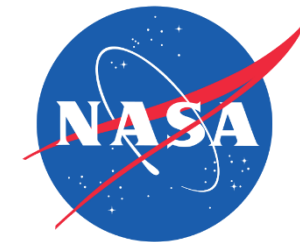
Build 3-electrode cells to understand effects on individual electrodes



Experimental Design

- Li/ CF_x - MnO_2 cells typically use LiClO_4 as an electrolyte salt
- Li/ CF_x cells typically use LiBF_4 as an electrolyte salt
- Two cells with 0.75 M **LiBF₄** in PC+DME (3:7 by vol.)
- Two cells with 0.75 M **LiClO₄** in PC+DME (3:7 by vol.)
- Subject one of each to 10 MRad
- Keep one of each for control

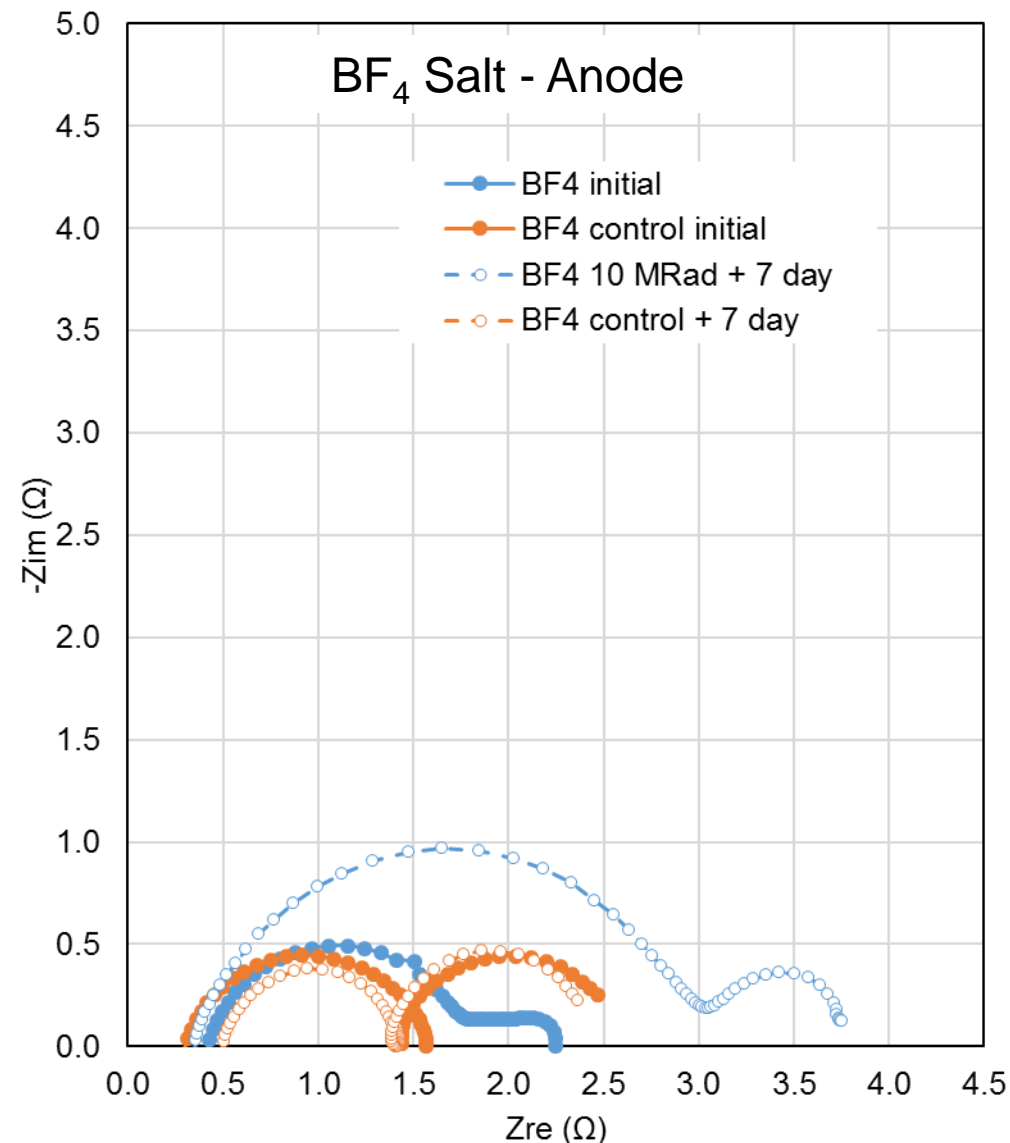
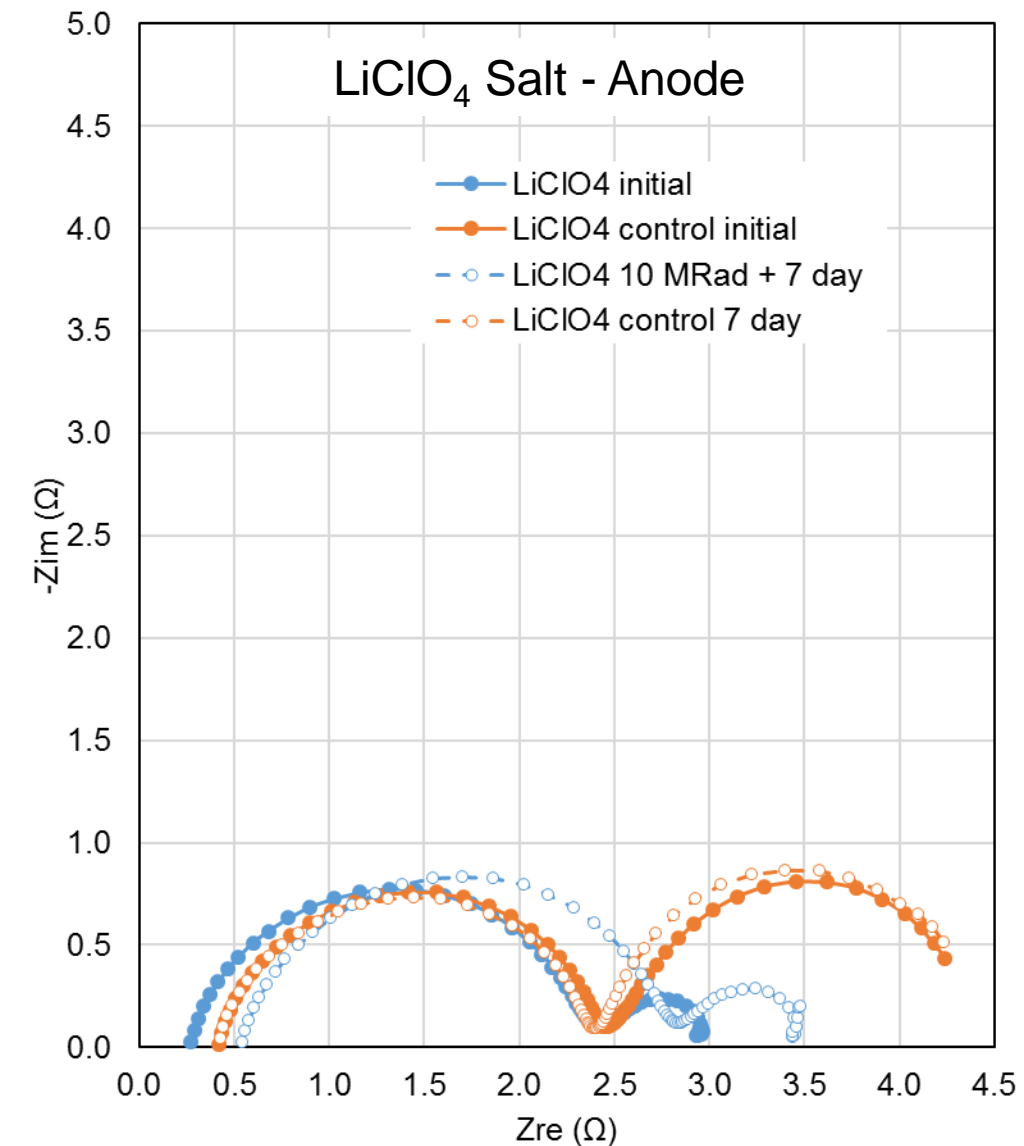
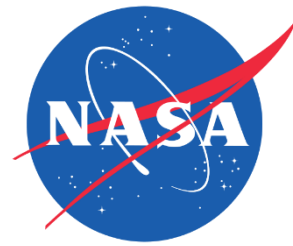
Film on cathode of Li/CF_x cell with LiClO₄ salt appears unaffected after 10 MRad



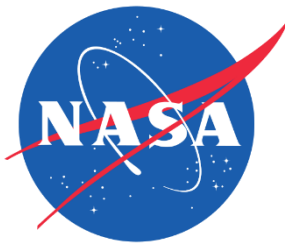
BF₄ salt leads to significant increase in “film” resistance on cathode

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Film on anode of Li/CF_x cell with LiClO_4 salt appears unaffected after 10 MRad

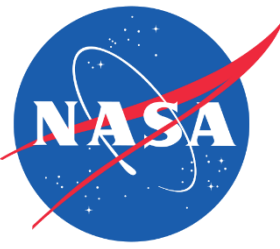


BF_4 salt leads to significant increase in “film” resistance on anode



Conclusions

- Li/CF_x cells provide the highest available specific energy
- Degradation of the cell has been observed in Li/CF_x D-cells
 - Increased “film” resistance
 - Increased low frequency resistance
 - Increased cell OCV
 - Lower energy
 - Lower capacity
- “Film” resistance grows in 3-electrode cells with LiBF_4 salt
 - Both anode and cathode are affected
- “Film” resistance remains constant in 3-electrode cells with LiClO_4 salt
 - Hope to incorporate other salts into prototype Li/CF_x D-cells



Acknowledgements

The work described here was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration (NASA), and was supported by the Planetary Science Division.